

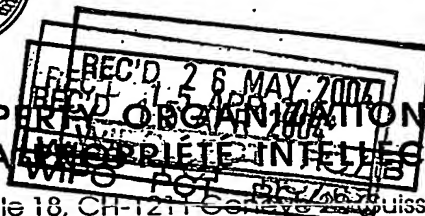
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International Application No. } PCT/IB 03 / 01472
Demande internationale n° }

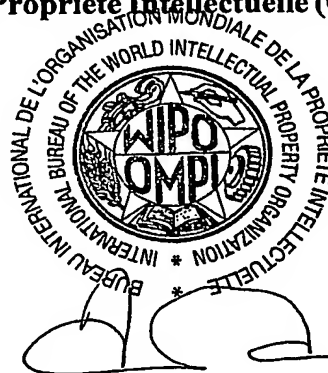
International Filing Date } 17 APRIL 2004
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(17.04.03)

Geneva/Genève, 27 APRIL 2004
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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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PCT/IB 03 / 0 1 4 7 2

International Application No.

17 APRIL 2003

(17.04.03)

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Box No. I TITLE OF INVENTION	
ALUMINIUM-WETTABLE CARBON-BASED BODY	
Box No. II APPLICANT <input type="checkbox"/> This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
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This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
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CRONIN, Brian MOLTECH S.A. Rte de Troinex 9 1227 CAROUGE SWITZERLAND	
Telephone No. +41 22 343 26 70	
Facsimile No. +41 22 342 97 15	
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Box No. VI PRIORITY CLAIM				
The priority of the following earlier application(s) is hereby claimed:				
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
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item (2)				
item (3)				
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<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.				
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* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):				
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<input type="checkbox"/> Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent			:
<input type="checkbox"/> Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application			:
<input type="checkbox"/> Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)			:
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Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:

(a) the following number of sheets in paper form:

request (including declaration sheets) : 5
 description (excluding sequence listing part) : 9
 claims : 5
 abstract : 1
 drawings : _____

Sub-total number of sheets : 20

sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) : _____

Total number of sheets : 20

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Marc Loosli (secretary of Brian Cronin - Agent)

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ALUMINIUM-WETTABLE CARBON-BASED BODY

Field of the Invention

The invention relates a carbon-based body having an aluminium-wettable surface. The body can be used as a component of an apparatus which during use contains
5 molten aluminium that comes into contact with the component, for example an aluminium electrowinning cell or an apparatus for treating molten aluminium.

Background of the Invention

The production, purification or recycling of
10 aluminium is usually carried out at high temperature in very aggressive environments, in particular in molten aluminium, molten electrolyte and/or corrosive gas. Therefore, the materials used for the manufacture of components exposed to such environments must be thermally
15 and chemically stable.

Graphite and other carbonaceous materials are commonly used for components, especially conductive components. Unfortunately, carbon components do not resist oxidation and/or corrosion and must be
20 periodically replaced.

Several proposals have been made to reduce wear of carbon components in such technologies to achieve a higher operation efficiency, reduce pollution and the costs of operation.

25 For the purification of molten metals, in particular molten aluminium, by the injection of a flux removing impurities towards the surface of the molten metal, it has been proposed to coat carbon components which are exposed to the molten metal with a coating of refractory
30 material as disclosed in WO00/63630 (Holz/Duruz).

In aluminium production, some components are exposed to molten fluoride-containing electrolyte, molten

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aluminium and/or anodically produced oxygen. In conventional Hall-Héroult cells these components are still made of consumable carbonaceous materials.

5 The use of titanium diboride and other RHM current-conducting elements to protect or replace carbon components in electrolytic aluminium production cells is described in US Patents 2,915,442, 3,028,324, 3,156,639, 3,215,615, 3,274,093, 3,314,876, 3,330,756, 3,400,061, 3,661,736, 4,093,524, 4,308,114, 4,466,996, 5,217,583,
10 5,310,476, 5,316,718, 5,364,513, 5,374,342, 5,618,403, 5,651,874, 5,728,466, 5,746,895 and 6,436,250.

Recently, the aluminium-wettability of RHM coatings has been significantly improved by the addition of aluminium-reactable metal oxides, such as iron, copper,
15 cobalt, nickel, zinc and manganese oxides, as disclosed in WO01/42168 (de Nora/Duruz), WO01/42531, (Nguyen/Duruz/de Nora), WO02/096830 (Duruz/Nguyen/de Nora) and WO02/096831 (Nguyen/de Nora).

Such RHM coated bodies have the following
20 attributes: excellent wettability by molten aluminium, resistance to attack by molten aluminium and cryolite, low cost, environmentally safe, ability to absorb thermal and mechanical shocks, durability in the environment of an aluminium production cell, and ease of production and
25 processing.

Summary of the Invention

An object of the invention is to provide a carbon body that is easy to manufacture and that has an aluminium-wettable surface.

30 A main object of the invention is to provide a carbon body that has the desired mechanical, physical, chemical, and electrochemical characteristics so that it can be used in a molten aluminium environment, in particular in an aluminium electrowinning cell or in an
35 apparatus for treating molten aluminium.

The invention relates to a carbon body having an aluminium-wettable outer part that is made of a carbon-rich mixture containing metal-based particles and carbon.

- 3 -

The metal-based particles are made of metal oxide particles and/or partly oxidised metal particles or a precursor thereof. The metal of the metal-based particles are selected from iron, copper, cobalt, nickel, zinc and manganese and combinations thereof. The metal oxide particles and/or partly oxidised metal particles are reactable with molten aluminium when exposed thereto to form a mixture of: aluminium oxide; the metal of said metal-based particles; and aluminium.

10 Carbon is an aluminium-repellent material. However, it has been found that when carbon material is mixed with an aluminium-reactable metal oxide and/or partly oxidised metal, molten aluminium reacts therewith to form alumina and the metal derived from the metal oxide and/or partly oxidised metal by transfer of oxygen from the metal oxide and/or partly oxidised metal to the aluminium. The metal derived from the metal oxide and/or partly oxidised metal may then be alloyed with unreacted molten aluminium. Hence, the presence of the aluminium-reactable metal oxide and/or partly oxidised metal promotes infiltration of aluminium by reaction therewith into the carbon material.

Moreover, alumina, aluminium and the metal derived from the metal oxide and/or partly oxidised metal form a mixture that remains within the carbon material, in particular at its surface, and maintains it wetted by aluminium after reaction.

It has surprisingly been observed that the carbon body with the aluminium-wettable outer part according to the invention is less exposed to corrosion by molten aluminium compared to a non-wettable carbon body, despite penetration of aluminium into the body's outer part.

Without being bound to any theory, it is believed that the reduced corrodability of the carbon body according to the invention has two causes. On the one hand, the mixture of alumina, aluminium and the metal derived from the metal oxide and/or partly oxidised metal, formed at the body's outer part is less reactive than pure aluminium. Hence carbon reacts less with this mixture than it does with pure aluminium to form

aluminium carbide. On the other hand, the aluminium layer that continuously wets the body's outer part during use inhibits exposure to the environment, e.g. cryolite, of the formed aluminium carbide and dissolution thereof into the environment.

The carbon body can be a fully manufactured body or a part-manufactured body that is subsequently, for example, subjected to a consolidation or conditioning treatment, e.g. a heat and/or aluminisation treatment.

10 The carbon-rich mixture is made predominantly of carbon, i.e. carbon is the mixture's main constituent.

15 The body can comprise an inner part that is substantially free of metal-based particles, the body's outer part having a thickness of 5 to 50 mm, in particular from 10 to 25 mm. Alternatively, the body comprises metal-based particles throughout.

20 In one embodiment, the metal-based particles are impregnated into the carbon body. In this case, the particles will be found in the body's pores, especially towards the body's surface. Typically, the carbon and the metal-based particles in the outer part are present in a weight ratio metal-based particles/carbon from 1/100 to 1/20, in particular from 1/50 to 1/25.

25 In another embodiment, the body's outer part is made of a heat treated mixture of the metal-based particles and particles of carbon. For example, the metal-based particles of the outer part are present in a weight ratio metal-based particles/carbon from 1/20 to 1/2, in particular from 1/8 to 1/4.

30 The outer part of the carbon body may comprise further particles of at least one additional metal compound. The additional metal compound(s) can be selected from refractory borides, silicides, nitrides, carbides, phosphides, oxides, aluminides, metal alloys, 35 intermetallics, and mixtures thereof, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum and molybdenum. Usually, the further particles and the metal-based particles of the outer part are present in a

weight ratio further particles/metal-based particles from 1/10 to 1/2.

5 The metal-based particles can be present in the body's outer part in an organic carrier, in particular selected from pitch, polyurethane, ethylene glycol, polyethylene glycol, resins, esters or waxes, and/or an inorganic carrier, in particular selected from colloidal and/or polymeric metal compounds of metals selected from aluminium, silicon, yttrium, cerium, thorium, zirconium, 10 tin, nickel, iron, chromium and magnesium which compounds form a metal oxide binder upon heat treatment.

15 The body can also be coated with an aluminium-wettable top coating which is free or substantially free of carbon. Examples of top coatings, in particular containing refractory borides and/or aluminium-reactable metal oxides, are disclosed in WO01/42168 (de Nora/Duruz), WO01/42531, (Nguyen/Duruz/de Nora), WO02/096830 (Duruz/Nguyen/de Nora) and WO02/096831 (Nguyen/de Nora).

20 The invention also relates to a carbon body having an aluminium-wetted outer part producible by exposing the above described body to molten aluminium. The outer part comprises a carbon-rich mixture containing: aluminium oxide; the metal of said metal-based particles; and 25 aluminium.

30 The invention further relates to a method of manufacturing a carbon body. The method comprises providing a mass of carbon and the above aluminium-reactable metal-based particles; adding the metal-based particles into the mass of carbon so as to form a carbon-rich mixture containing the metal-based particles; and consolidating by heat treatment the metal-based particles in the carbon mass to form an aluminium-wettable outer part of the carbon body which outer part is made of a 35 carbon-rich mixture containing the metal-based particles.

As mentioned above, the metal-based particles can be impregnated into the outer part of the carbon body that forms the carbon mass. The metal-based particles are then

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consolidated in the carbon body's outer part by heat treatment.

Alternatively, the metal-based particles are mixed with carbon particles that form the carbon mass, the
5 mixed carbon particles and metal-based particles being then consolidated by heat treatment to form the outer part of the carbon body.

For instance, a layer of the carbon particles and the metal-based particles can be consolidated on a
10 substrate. The substrate can be either baked, or non-baked or part-baked in which case the layer and the carbon substrate can be consolidated together by heat treatment. For example, the layer of the particle mixture can be formed by co-extrusion followed by heat treatment.

Alternatively, the carbon particles and the metal-based particles can be consolidated to form a self-sustaining body.
15

The heat treatment can be carried out at a temperature above 200°-450°C and usually below 3000°C.
20 Typically, consolidation of the particle mixture takes place at a temperature from about 250° to 650°C. However, the heat treatment can also take place at temperatures up to around 2000° to 3000°C, especially when a carbon green, e.g. a substrate, is consolidated at the same
25 time.

The above-mentioned further particles of at least one additional metal compound may be added into the mass of carbon.

Typically, the metal-based particles are provided in
30 a liquid carrier. The liquid carrier can comprise an organic carrier and/or an inorganic carrier as mentioned previously.

Furthermore, the aluminium-wettable outer part can be exposed before or during use to molten aluminium to
35 react the outer part's metal-based particles with molten aluminium and wet the outer part by aluminium.

Another aspect of the invention relates to a carbon-rich particle mixture for forming upon heat treatment a self-sustaining body or a layer of carbon that contains the metal oxide and/or partly oxidised metal. The particle mixture comprises carbon particles and the above described metal-based particles.

A further aspect of the invention relates to a component of an apparatus that during use contains molten aluminium. The component comprises a body with an outer part containing the metal-based particles as described above.

Yet another aspect of the invention relates to an apparatus that during use contains molten aluminium and comprises the above component.

This apparatus can be a cell for the electrowinning of aluminium, the above-mentioned component being a cathodic component, a cell bottom component or a sidewall component. Examples of aluminium electrowinning cells are for example disclosed in US Patents 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,358,393 and 6,436,273 (both de Nora/Duruz). Further cells are disclosed in PCT applications WO99/02764 (de Nora/Duruz), WO00/40781, WO00/40782 (both de Nora), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz), WO01/31088, WO02/070783, WO02/070785, WO02/097168 and WO02/097169 (all de Nora).

The apparatus may be an apparatus for treating molten aluminium, the above component being exposed during use to molten aluminium. Examples of such apparatus are disclosed in WO00/63630 (Holz/Duruz).

Yet a further aspect of the invention relates to a method of operating the above apparatus. During operation the component is exposed to molten aluminium. When the apparatus is an aluminium electrowinning cell, the method comprises electrowinning aluminium which comes into contact with the component. When the apparatus is an apparatus for treating molten aluminium, the method comprises treating molten aluminium which comes into contact with the component.

Detailed Description

The invention will be further described in the following examples.

Example 1

5 A graphitised carbon block was made aluminium-wettable by impregnation with an iron compound and then the block was aluminised as follows.

10 An impregnation solution was prepared by mixing an amount of 100 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 50 g H_2O (density 1.4 g/cm³). The carbon block was impregnated by dipping into this solution at room temperature for 10 to 15 min. The carbon block was dried for 24 hours in air at 60 to 80°C and then heat treated in air between 250° and 500°C. During the heat treatment, the $\text{Fe}(\text{NO}_3)_3$ was transformed
15 into iron oxide and the block's colour turned red-brown (indicating the presence of Fe_2O_3).

 The block was impregnated over a depth of about 2.5 to 3 cm. The impregnated part of the carbon block contained about 1.5 weight% Fe_2O_3 .

20 The impregnated carbon block was then dipped into a bath of molten aluminium at a temperature of 940°C. After 12 hours the carbon block was extracted from the molten aluminium. The block was wetted by an adherent thin layer of molten aluminium. Aluminium had impregnated the
25 block's entire surface over a depth of at least 0.2 mm and locally up to about 20 mm and had partly alloyed with iron upon reaction of aluminium and the block's iron oxide (forming alumina and iron metal).

Example 2

30 An aluminium-wettable graphitised carbon cathode block was aluminised by the method of Example 1.

 The aluminised block was then tested in a laboratory aluminium electrowinning cell containing an electrolyte made of 11 wt% aluminium fluoride (AlF_3), 9.6 wt% alumina
35 (Al_2O_3), 5 wt% potassium fluoride (KF), 4 wt% CaF, the balance being cryolite (Na_3AlF_6). An electrolysis current

was passed through the block at a cathode current density of about 0.5 A/cm².

After 80 hours, the electrolysis was interrupted and the cathode block examined. The block was still perfectly wetted by a film of molten aluminium. The penetration of the block by molten aluminium did not significantly change during operation in the cell.

Example 3

An aluminium-wettable carbon-based body was prepared and aluminised as follows.

A mixture of iron oxide and carbon was prepared by mixing 18 g of graphite powder (with a particle size below about 100 to 200 micron), 3 g iron oxide powder (with a particle size below about 45 micron) and 12 g pitch.

The mixture was cast into a plastic mould and allowed to dry for 12 hours to form a carbon-based block that was then heat treated for 2 hours at 450°C for consolidation.

After heat treatment, the carbon-based block was dipped into a bath of molten aluminium at a temperature of 940°C. After 12 hours the carbon block was extracted from the molten aluminium. The block was wetted by an adherent thin layer of molten aluminium and impregnated to a depth of about 0.2 mm by aluminium that had reacted and alloyed with iron upon reaction of aluminium and the block's iron oxide.

Example 4

An aluminised carbon-based body manufactured as in Example 3 was used as a cathode in a laboratory cell as in Example 2 and behaved similarly.

CLAIMS

1. A carbon body having an aluminium-wettable outer part that is made of a carbon-rich mixture containing metal-based particles and carbon, the metal-based
5 particles being made of metal oxide particles and/or partly oxidised metal particles or a precursor thereof, the metal of the metal-based particles being selected from iron, copper, cobalt, nickel, zinc and manganese and combinations thereof, the metal oxide particles and/or
10 partly oxidised metal particles being reactable with molten aluminium when exposed thereto to form a mixture of: aluminium oxide; the metal of said metal-based particles; and aluminium.
2. The body of claim 1, which comprises an inner part
15 that is substantially free of metal-based particles, and wherein said outer part has a thickness of 5 to 50 mm, in particular from 10 to 25 mm.
3. The body of claim 1, which comprises metal-based particles throughout.
- 20 4. The body of any preceding claim, wherein the metal-based particles are impregnated into the carbon body.
5. The body of claim 4, wherein the carbon and the metal-based particles in the outer part are present in a weight ratio metal-based particles/carbon from 1/100 to
25 1/20, in particular from 1/50 to 1/25.
6. The body of any one of claims 1 to 3, wherein the outer part is made of a heat treated mixture of the metal-based particles and particles of carbon.
7. The body of claim 6, wherein the carbon and the
30 metal-based particles of the outer part are present in a weight ratio metal-based particles/carbon from 1/20 to 1/2, in particular from 1/8 to 1/4.

8. The body of any preceding claim, wherein the outer part of the carbon body comprises further particles of at least one additional metal compound.
9. The body of claim 8, wherein said at least one additional metal compound is selected from refractory borides, silicides, nitrides, carbides, phosphides, oxides, aluminides, metal alloys, intermetallics, and mixtures thereof, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum and molybdenum.
10. The body of claim 8 or 9, wherein said further particles and said metal-based particles of the outer part are present in a weight ratio further particles/metal-based particles from 1/10 to 1/2.
11. The body of any preceding claim, wherein the metal-based particles are present in the outer part in an organic carrier, in particular selected from pitch, polyurethane, ethylene glycol, polyethylene glycol, resins, esters or waxes.
12. The body of any preceding claim, wherein the metal-based particles are present in the outer part in an inorganic carrier, in particular selected from colloidal and/or polymeric metal compounds of metals selected from aluminium, silicon, yttrium, cerium, thorium, zirconium, tin, nickel, iron, chromium and magnesium which compounds form a metal oxide binder upon heat treatment.
13. The body of any preceding claim, comprising an aluminium-wettable top coating which is free or substantially free of elemental carbon and organic carbon compounds.
14. A carbon body having an aluminium-wetted outer part producible by exposing the body of any preceding claim to molten aluminium, the outer part comprising a carbon-rich mixture containing: aluminium oxide; the metal of said metal-based particles; and aluminium.
15. A method of manufacturing a carbon body comprising:
- providing a mass of carbon;
 - providing metal-based particles made of metal oxide particles and/or partly oxidised metal particles or a

- heat-convertible precursor thereof, the metal of the metal-based particles being selected from iron, copper, cobalt, nickel, zinc and manganese and combinations thereof, the metal oxide particles and/or partly oxidised metal particles being reactable with molten aluminium when exposed thereto to form a mixture of: aluminium oxide; the metal of said metal-based particles; and aluminium;
- 5 - adding the metal-based particles into the mass of carbon so as to form a carbon-rich mixture containing the metal-based particles; and
- 10 - consolidating by heat treatment the metal-based particles in the carbon mass to form an aluminium-wettable outer part of the carbon body which outer part is made of a carbon-rich mixture containing the metal-based particles.
- 15
16. The method of claim 15, wherein the metal-based particles are impregnated into the outer part of the carbon body that forms the carbon mass, the metal-based particles being then consolidated in the carbon body's outer part by heat treatment.
- 20
17. The method of claim 15, wherein the metal-based particles are mixed with carbon particles that form the carbon mass, the mixed carbon particles and metal-based particles being then consolidated by heat treatment to form the outer part of the carbon body.
- 25
18. The method of claim 17, wherein a layer of the carbon particles and the metal-based particles is consolidated on a substrate.
- 30 19. The method of claim 18, wherein said layer is consolidated on a baked carbon substrate.
20. The method of claim 18, wherein the substrate is a non-baked or part-baked carbon substrate, said layer and substrate being consolidated together by heat treatment.
- 35 21. The method of claim 20, wherein the substrate and the layer of the particle mixture are formed by co-extrusion followed by heat treatment.

22. The method of claim 17, wherein the carbon particles and the metal-based particles are consolidated to form a self-sustaining body.

5 23. The method of any one of claims 14 to 22, comprising adding into the mass of carbon further particles of at least one additional metal compound.

10 24. The method of claim 23, wherein said at least one additional metal compound is selected from refractory borides, silicides, nitrides, carbides, phosphides, oxides, aluminides, metal alloys, intermetallics, and mixtures thereof, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum and molybdenum, and precursors thereof.

15 25. The method of claim 23 or 24, wherein said further particles are provided in a mixture with said metal-based particles which is added into the carbon mass.

26. The method of any one of claim 14 to 25, wherein the metal-based particles are provided in a liquid carrier.

20 27. The method of claim 26, wherein the liquid carrier comprises an organic carrier, in particular selected from pitch, polyurethane, ethylene glycol, polyethylene glycol, resins, esters or waxes.

25 28. The method of claim 26 or 27, wherein the liquid carrier comprises an inorganic carrier, in particular selected from colloidal and/or polymeric metal compounds of metals selected from aluminium, silicon, yttrium, cerium, thorium, zirconium, tin, nickel, iron, chromium and magnesium which compounds form a metal oxide binder upon heat treatment.

30 29. The method of any one of claims 14 to 28, comprising applying onto the metal-based particle-containing outer part of the carbon body, an aluminium-wettable top coating which is free or substantially free of elemental carbon and organic carbon compounds.

35 30. The method of any one of claims 14 to 29, comprising exposing the aluminium-wettable outer part to molten

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aluminium to react said metal-based particles with molten aluminium and wet the outer part by aluminium.

31. A carbon-rich particle mixture for forming upon heat treatment a self-sustaining body or a layer of carbon that contains metal oxide and/or partly oxidised metal, the particle mixture comprising carbon particles and metal-based particles made of a metal oxide and/or a partly oxidised metal or a precursor thereof, the metal from the metal-based particles being selected from iron, copper, cobalt, nickel, zinc and manganese and combinations thereof, the metal-based particles being reactable with molten aluminium when exposed thereto to form a mixture of: aluminium oxide; the metal of said metal-based particles; and aluminium.
32. A component of an apparatus that during use contains molten aluminium, the component comprising a body as defined in any one of claims 1 to 13.
33. An apparatus that during use contains molten aluminium, and having a component as defined in claim 32.
34. The apparatus of claim 33, which is a cell for the electrowinning of aluminium, said component being part of a cathode, a cell bottom or a sidewall.
35. The apparatus of claim 33, which is an apparatus for treating molten aluminium, said component being exposed during use to molten aluminium.
36. A method of operating an apparatus as defined in any one of claims 33 to 35, wherein during operation said component is exposed to molten aluminium.
37. The method of claim 36, wherein the apparatus is an aluminium electrowinning cell, said method comprising electrowinning aluminium which comes into contact with said component.
38. The method of claim 36, wherein the apparatus is an apparatus for treating molten aluminium, said method comprising treating molten aluminium which comes into contact with said component.

ABSTRACT

A carbon body has an aluminium-wettable outer part that is made of a carbon-rich mixture containing aluminium-reactable metal-based particles and carbon. The metal-based particles are made of metal oxide particles and/or partly oxidised metal particles. The metal of the metal-based particles is selected from iron, copper, cobalt, nickel, zinc and manganese. The carbon body can be used in an aluminium electrowinning cell, e.g. as a cathode, or in an apparatus for treating molten aluminium and is wetted by molten aluminium during use.